MINAR International Journal of Applied Sciences and Technology
ISSN: 2717-8234
Article type: Research Article

Received:05/05/2022 **Accepted:**23/05/2022 **Published:** 01/09/2022

SYNTHESIS OF TRIPODAL BORATE LIGAND WITH NI(II) AND CU(II) COMPLEXES

Asmaa Mohammed Noori KHALEEL [1]

University of Baghdad, Iraq

Abstract

New tripodal ligand sodium[2,2',2''-((λ4-boranetriyl)tris(1 H-indole-1,3-diyl))tri acetic acid]hydrate (BIAA) was synthesized by the reaction of heteroauxin (indole -3- acetic acid) with sodium tetrahydroborate in 3:1 mole ratio. The ligand was characterized by elemental analysis, spectral studies such as FTIR, UV-Vis., 1HNMR and thermal analysis spectra, the results were agreement with the proposed structure. The coordination property of the ligand was studied through preparation of two metal complexes with Ni(II) and Cu(II) in 2:1 (L:M) mole ratio. Depending on elemental analysis, FTIR , UV-Vis. spectra, magnetic susceptibility measurements , atomic absorption and molar conductivity of metal complexes ,the suggested geometry of nickel and copper complexes were octahedral structures.

Keywords: Tripodal ligands , borate ligands.

http://dx.doi.org/10.47832/2717-8234.12.20

[1] asmaa.m@sc.uobaghdad.edu.iq

This article has been scanned by **iThenticat** No **plagiarism** detected

Introduction

Borate-based ligands were used in coordination chemistry and have gained significant attention such as scorpionate ligands. The substituted polypyrazolyl borates have been excellent used for the biomimetic modelling of nitrogen-rich active sites, as a facial coordination and allow mimicking of a tetrahedral geometry [1].

Tripodal ligands (as tri- and tetra dentate ligands) used in the areas of coordination chemistry and homogeneous catalysis. Various studies shown that the tripodal ligands can be classified into two main groups: flexible and rigid tripodal ligands. The donor groups in the tripodal ligands lead to complexation with a good formation constant.The donor groups in tripodal ligands are usually donor soft groups that are connected to nitrogen atoms and the molecule resemble a flexible tripod [2].

The tripodal ligands can act as receptors for different chemical species: anions, or cations and anions in the same time, transition metal ions, lanthanide and actinide ions. The thermodynamic stability of the host–guest complexes makes from the tripodal ligands good candidates for biomedical applications as sequestering agents for iron, aluminium or actinide ions [3].

Tris (2 pyridyl) methylamine (tpm) iono phore as a basic part for the potential response of ion selective electrodes (ISEs) and has been used to prepare the membrane [2]

The tripodal *tris* (2-mercapto-1-R–imidazolyl) hydroborato ligand [Tm^R] (Figure 1) and its selenium complex [Tse^R], supply useful rostrum for organometallic and bioinorganic aspects of the chemistry of zinc, cadmium and mercury in (sulfur and selenium)-rich coordination environments. The tridentate [Tm^R] ligand supply [S_3] donor configuration that is use for mimicking aspects of zinc-enzymes and proteins that have sulfur-rich active sites [4]. The S-donor methimazolyl borates Tm, analogous to the pyrazole borates, also show some differences in their behaviour, the S-donor atom is exo- to the heterocycle ring, the methimazolylborates take eight-membered chelates, whereas the pyrazole borates take six-membered chelates. [5]

N-donor ligands, hydrido *tris*(pyrazolyl) borate (Tp) (Figure 1) and hydrido *tris*(3,5-dimethylpyrazolyl)borate (Tp*) are the basis for an extensive chemistry with metallic elements [5]. Several cobalt complexes with tripodal chelating ligands Tp and Tp* were synthesized as the homo scorpionates under different conditions such as isolation the product after stirring or after stored in the air and from crystallization of mother liquid [5,6].

The oxygen derivatives of [Tp^{iPr2}]Cu and [Tp^{tBu}]Cu were dimeric with a μ-η^2:η^2-peroxo bridge, the 3-*tert*-butyl pyrazole substituents in the latter perform a monomer, with side-on superoxide ligation. These ligands with strong field donors such as *tris*(phosphino) borates ($PhBP_3$) and *tris*(carbene) borates with hybrid ligands containing two or three different heteroatom donors. Less common tripodal ligands with sulfur heteroatom donors contain the poly(thioether) borates (Tt) (Figure 1) [7]

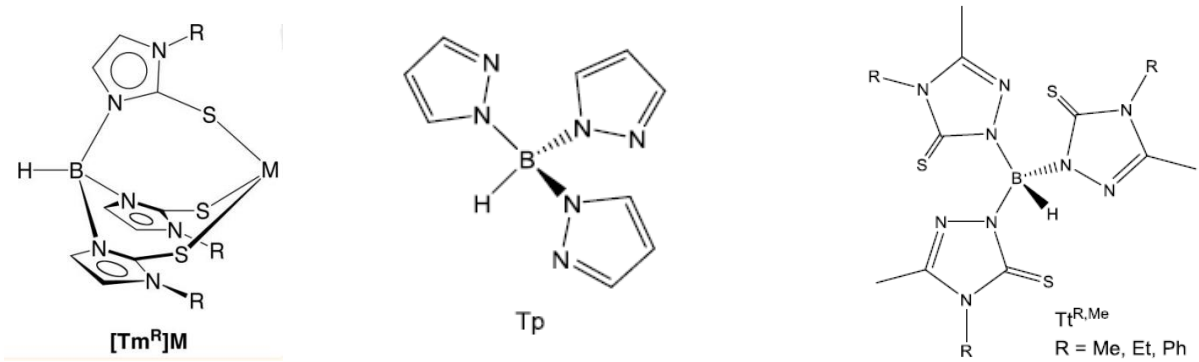

Figure 1: Examples of Scorpionate Ligands

The indole-3-acetic acid (IAA) (auxin) is a plant hormone for regulates plant growth and development, also plays plays arole in plant microbe interactions [8].. It has been found the different fungi,bacteria, and algae are capable of producing physiologically active amounts of IAA [9]. The interaction of IAA with cobalt (II), copper (II) and nic kel (II) in ethanol and in solid state were studied [10]. Also the complexes with Fe(III) and Zn(II), Al(III), Bi(III), Sb(III), Sn(II) and Pb(II) were synthesized [11,12, 13]

In the present work, new tripodal borate ligand (BIAA) was synthesized with Nickel and Copper metals to form the new complexes. All synthesized compounds were characterized using physicochemical and spectral methods. Thermal stability of the ligand and coordination properties of complexes were also studied.

Experimental Part

All chemicals were used as received without further purification.

Synthesis of the tripodal ligand (BIAA) $Na[BH(IAA)_3]3.5H_2O$

Synthesis of the ligand carried out depending on the literature [14,15]with modified from $NaBH_4$ and indole acetic acid (IAA) in 1:3 mole ratio. The solution of $NaBH_4$ (0.05 g, 1.321 mmol) in 6ml toluene was added to a hot solution of IAA (0.6946 g, 3.965 mmol) in 8ml toluene, the mixture was heated under reflux for 15 hour with vigorous stirrer, the crystal product washed with hot toluene, recrystallization from the mixture (aceton:H_2O 5:1) and washed with petroleum ether, the final product was greenish gray crystals.

Synthesis of Nickel (II) and Copper (II) Complexes

The ethanolic solution of ligand and metal salt in 2:1 mole ratio was stirred at room temperature for 6 hours and the color changed from green to brown Part of solvent was evaporated ,the brown product appeared after adding acetone, standing overnight and finally isolated the product.

(Ligand (0.20g, 0.318mmol), $NiCl_2.6H_2O$ (0.0378g, 0.159mmol), $CuCl_2$ (0.0213g, 0.159mmol) in 9ml ethanol).

Results and Desiccation

The molecular formulae, physical properties, elemental analysis and metal content data illustrated in (Table 1)

Table 1: Analysis data of the tripodal ligand and its metal complexes

Comp.	molecular formulae	M.wt g.mol^{-1}	m.p (°C)	% Yield	Color	Elementa Micro Analysis Found (Calc.)			% Metal content
						C%	H%	N%	
Ligand (BIAA)	$Na[BC_{30}H_{25}N_3O_6]3.5H_2O$	619.8	140-142	73.93	Greenish gray	57.46 (58.08)	5.29 (5.16)	6.14 (6.77)	-
C_1 Ni(II)	$[B_2C_{60}H_{62}N_6O_{18}Ni_3Cl_4]6H_2O$	1601.67	> 280	44.68	Light brown	44.51 (44.95)	4.36 (4.62)	4.53 (5.24)	(10.15) (10.99)
C_2 Cu(II)	$[B_2C_{60}H_{62}N_6O_{18}Cu_3Cl_4]9H_2O$	1670.22	> 280	31.51	Dark brown	42.26 (43.10)	4.18 (4.78)	4.34 (5.02)	10.32 (11.41)

Infrared spectroscopy

The spectrum of ligand showed band at 3549 cm^{-1} which assigned to stretching vibration of lattice water, in complexes this band appeared at 3600 and 3614 cm $^{-1}$(Table 2) in Ni and Cu complexes respectively [16]. Broad band appeared at 2966-3124 cm^{-1} due to stretching vibration of OH group[17] this band appeared at higher frequency in complexes as a result of coordination to metal ions through OH group. The stretching vibration of carboxylic carbonyl group (υC=O)appeared at 1701cm^{-1} [10,11]and υB-N appeared at (1458-1463 cm $^{-1}$) [18], these bands not changed in complexes while the stretching vibration of B-H(υB-H) appeared at (2335-2360 cm^{-1})[18] and changed in complexes as a result of a gostic interaction. The spectra of complexes showed low frequency bands which assigned to υM-O and υM-Cl (Table 2) [19, 20].

Table 2|: The FT-IR data of the BIAA ligand and its metal complexes

Compounds	υH_2O Lattice (coord.)	υOH	υB-H	υC=O	υB-N	υM-O	υM-Cl
BIAA Ligand	3549	2966-3124	2360	1701	1458	-	-
C_1 (Ni (II))	3600 (740 , 800)	3190-3481	2335	1703	1463	500	273
C_2 (Cu(II))	3614 750 , 810) (	3352-3442	2350	1705	1460	480	223

Thermal Analysis (TGA & DTG)

The thermal study of the BIAA ligand was carried out by TGA and DTG analysis (Figure 2) using Helium as inert gas in rate 20ml /min . The suggested structure of the ligand has confirmed by obtaining a good agreement between practical and theoretical percentage of

mass loss (Table 3) . The results showed that percentage of residue was 21.76% at 850°C and this indicates the stability of BIAA ligand[16].

Table 3: Thermal decomposition of the BIAA ligand

compound	**Steps**	**DTG of the Decomposition °C**	**Suggested formula of loss**	**Mass loss% Cal. (Found.)**
BIAA Ligand $Na[BC_{30}H_{32}N_3O_{9.5}]$ 619.8 g/mol	1	93.11	$0.6H_2O$	(0.65) 1.74
	2	227.31	$2.9H_2O$	8.42(7.53)
	3	344.73	Na , $C_{10}H_8NO_2$,$C_3H_3O_2$, C_6H_4, CH	57.59(57.48
	4	653.39	$C_2H_3O_2$, BH, H	11.58(12.55)
	Residue	850	$C_8H_4N_2$	20.65(21.76)

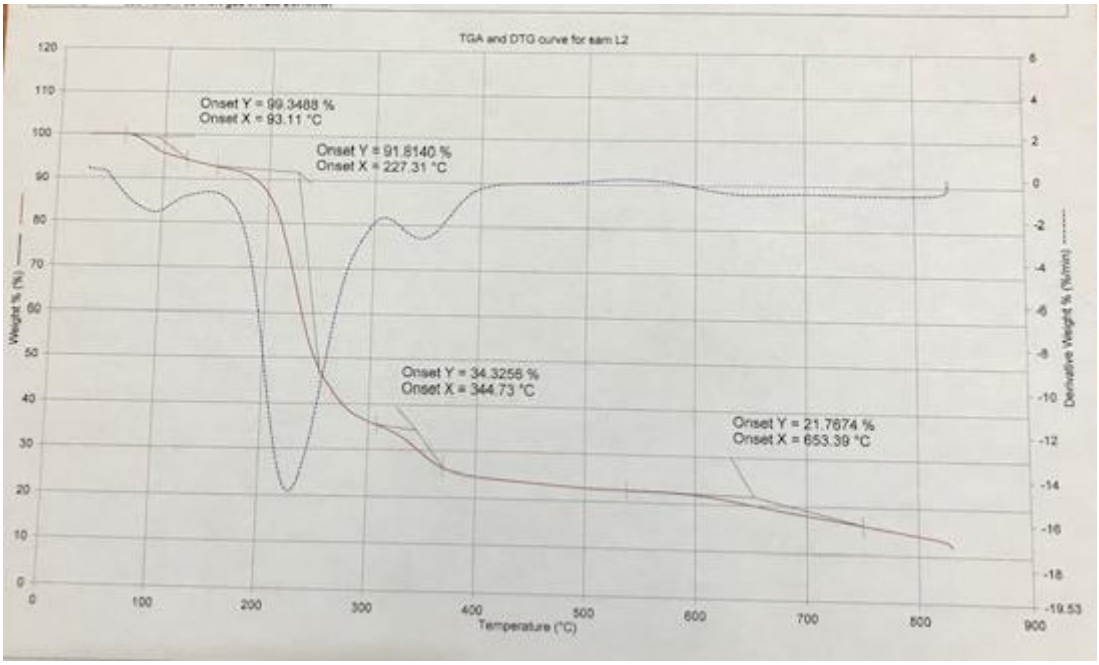
TGA and DTG curve for sam L2
Onset Y = 99.3488 %
Onset X = 93.11 °C
Onset Y = 91.8140 %
Onset X = 227.31 °C
Onset Y = 34.3256 %
Onset X = 344.73 °C
Onset Y = 21.7674 %
Onset X = 653.39 °C
Weight % (%)
Derivative Weight % (%/min)
Temperature (°C)

Figure 2: The thermogram of the BIAA ligand

^{1}H NMR spectrum

The ^{1}H NMR spectra of the ligand (Figure 3) was recorded in DMSO .The chemical shifts and peak assignments are given in (Table 4) .The peak appeared at δ = 10.88 ppm due to

proton of carboxylic OH [17]. Peak observed at δ 8.42 ppm which assigned to proton of NCH [21].

The spectrum exhibited multiple signal of aromatic protons which were observed in the chemical shift range (δ= 7.52-6.94 ppm) [17] . The spectra showed a peak at range δ= 3.71-3.40 ppm attributed to lattice H_2O [17] , B-H proton [14] and CH_2 protons [21]. The peak at δ 2.5 ppm was attributed to DMSO [17].

Table 4: Chemical shifts and assignments of the BIAA ligand

Chemical shift δ (ppm)	Assignments
(10.88,3H, s)	OH proton
(8.42, 3H, s)	NCH proton
(7.52-6.94, 12H, m)	Aromatic protons
(3.71-3.40, 13H, s)	H_2O, B-H and CH_2 protons

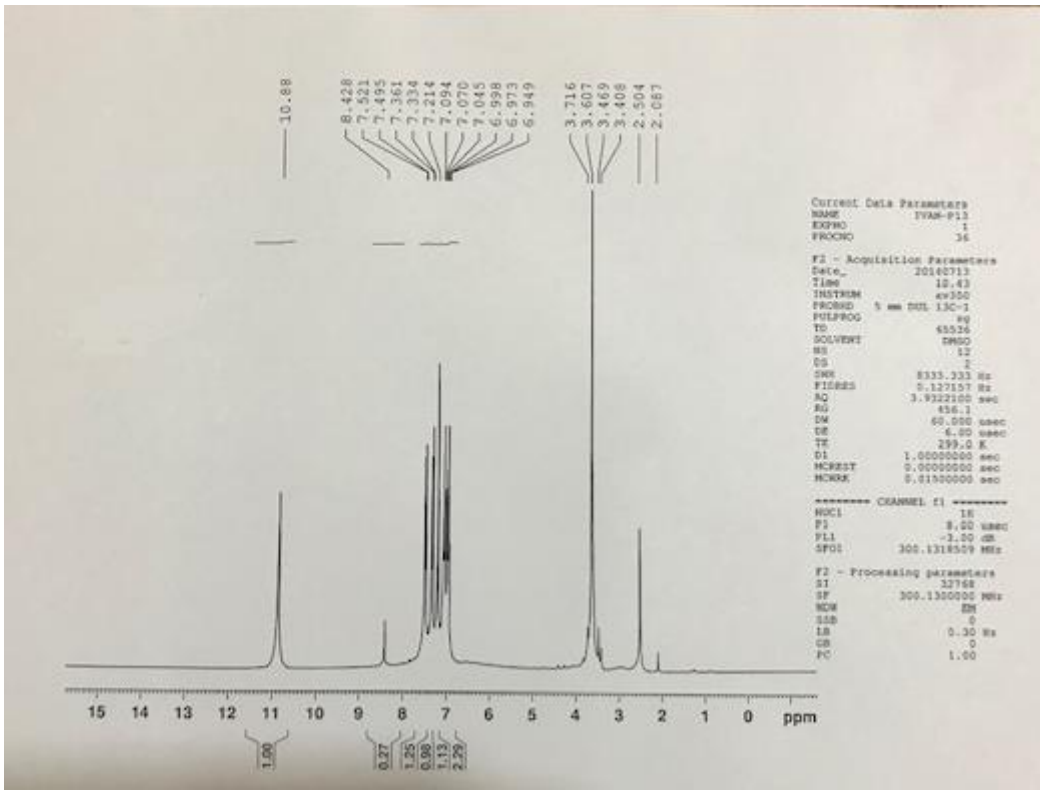

Figure 3: ^{1}HNMR spectrum of the BIAA ligand

Electronic Spectra, Magnetic Susceptibility and Conductivity Measurements

The electronic spectrum of the ligand in DMSO showed a high intensity band at 290 nm (34482 cm^{-1}) due to π ⟶ π* transition ,this band was shifted to higher frequency in complexes as a result of coordination with metal ions and low intensity band at 340 nm (29411 cm^{-1})due to n ⟶ π* transition.

The spectrum of Nickel complex (Figure 4A) was exhibited the following bands|: 260 nm(38461 cm^{-1}) , 310 nm (32258 cm^{-1}), 420nm (23809 cm^{-1}) and 980nm (10204 cm^{-1}) which assigned to π ⟶π*, n ⟶π* , $(\upsilon_3)\ ^3A_2g \longrightarrow\ ^3T_1g(p)(CT)$, $(\upsilon_1)\ ^3A_2g \longrightarrow\ ^3T_2g$ respectively

for octahedral geometry of Ni(II) complexes [22,23] . The spectrum of copper complex (Figure 4B) showed the following bands | : 284 nm (35211 cm^{-1}), 350 nm (28571 cm^{-1}) , 400nm (25000 cm^{-1}), 670 nm (14925 cm^{-1}) , 990 nm (10101 cm^{-1}) which assigned to

$\pi \longrightarrow \pi^*$, $n \longrightarrow \pi^*$, (L $\longrightarrow$ M) charge transfer C.T , (υ_2) $^2B_1g \longrightarrow {}^2B_2g$ and (υ_1) $^2B_1g \longrightarrow {}^2A_1g$ respectively for octahedral geometry of Cu(II) complexes[16, 23].

The molar conductivities of nickel and copper complexes were 0.124 and 0.064 $S.mol^{-1}.cm^2$ and this assigned to nonelectrolyte behavior of complexes . The magnetic moment of Ni(II) and Cu(II) as polynuclear complexes were µeff = 5.75 and 2.462 M.B for Ni and Cu complexes respectively for octahedral geometries and these results assigned to noninteracting metal centers of polynuclear complexes [24]

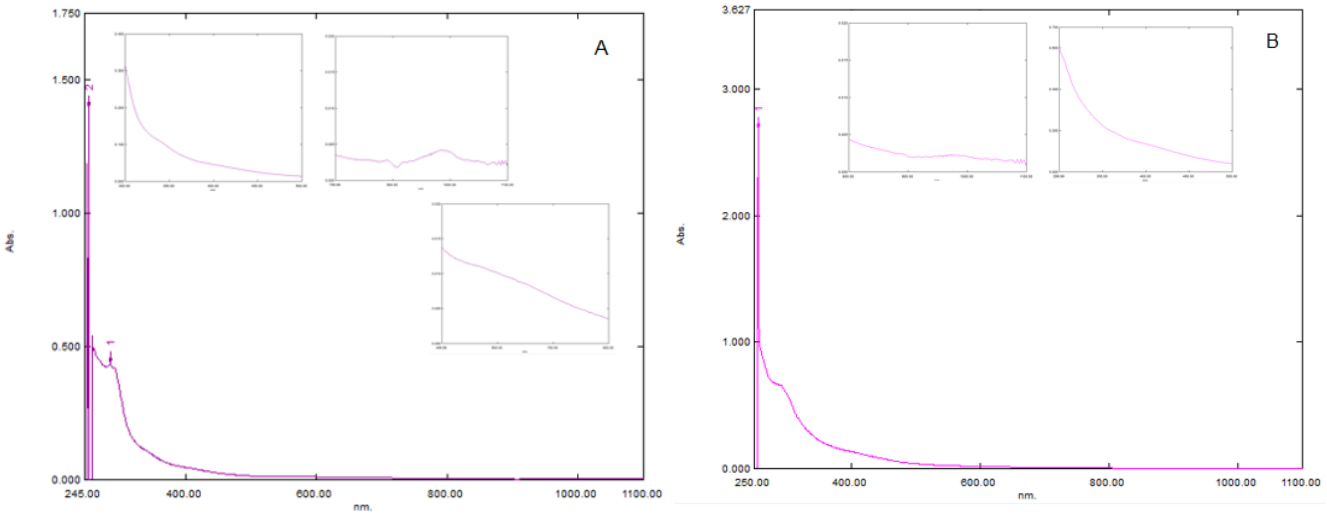

Figure 4: A-Electronic spectrum of Ni(II) complex , B- Electronic spectrum of Cu(II) complex

Conclusion

In this work, the new ligand (Figure 5)and its complexes with Ni(II) and Cu(II) metal ions (Figure 6)were synthesized and characterized by spectral and chemo physics methods. Based on the results of these techniques, the structures of new compounds was suggested and the complexes were octahedral geometry. Thermal stability Study of the ligand showed that 21.76 % from the ligand was stable up to 850 °C. The coordination properties study of metal complexes showed coordination of metal ions with H_2O, OH(acetic acid), Cl and M....H as agostic interactions. This multiple coordination due to formation of polynuclear complexes.

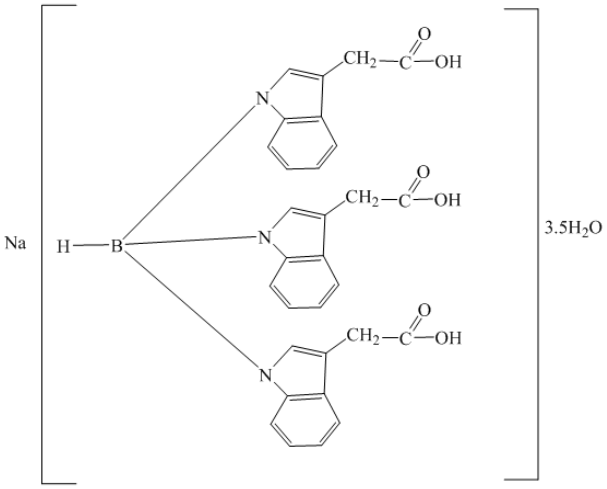

Figure 5: The suggested structure of BIAA ligand

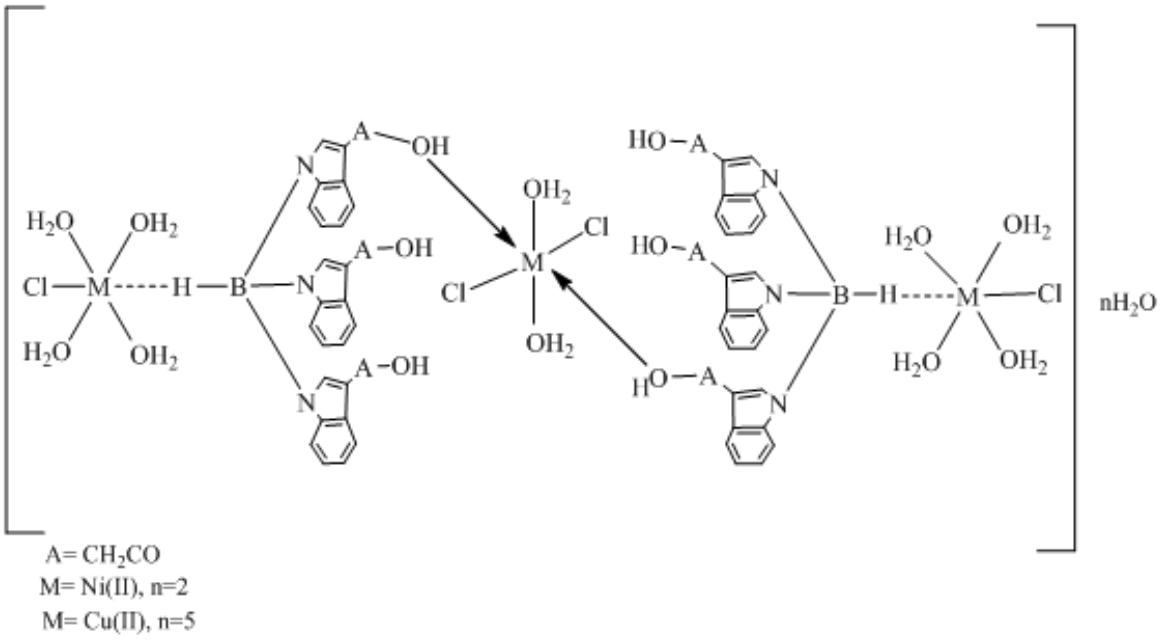

Figure 6: The suggested structures of Ni(II) and Cu(II) complexes

References

1-Michael T., Melanie R., Simon G., Klaus Z., Ferdinand B. and Nadia C. Mosch-Z,"Mono- and Hexanuclear Zinc Halide Complexes with Soft Thiopyridazine Based Scorpionate Ligands" ,Inorganics, 7(2), 24,(2019)

2- Majid R., Lee Y.H., Anuar K., Saeid A., Yadollah A. and Hossein J., "Immobilization of tris(2 pyridyl) methylamine in a PVC-Membrane Sensor and Characterization of the Membrane Properties" Chemistry Central Journal, 6:40 (2012)

3-Elena V. and Augustin M.M. " Synthesis and crystal structuresof a tripodal ligand derived from 4,4'-Dihydroxybiphenyl and its Gadolinium(III) mononuclear complex" Rev.Roum.Chim.,58(9-10),823-828 (2013)

4-Gerard P. ,"Applications of tripodal [S_3] and [Se_3] L_2X donor ligands to zinc, cadmium and mercury chemistry: organometallic and bioinorganic perspectives" New J.Cem.,31(12),1996-2014 (2007)

5-John R., Mark D.S. **,** "Chemistry of the *p*-block elements with anionic scorpionate ligands", Coordination Chemistry Reviews,Vol.297-298,181-207(2015)

6-Zhang B. , [Ph.D. Thesis]," *Synthesis, Properties, and Reaction Behavior of Cobalt and Copper Organometallic Complexes with Chelating Ligands*", Darmstadt, Technische Universität,(2013)

7-Charles G. R., "Coordination chemistry of poly(thioether)borate ligands" , Coord Chem Rev., 254(15-16): 1815–1825(2010).

8-Arnaud-T., Djami-T., Zipeng A. L.,a Paul S.,Melanie J. F., Barbara N. K.,"Identification of Indole-3-Acetic Acid-Regulated Genes in Pseudomonas syringae pv. tomato Strain DC3000", Journal of Bacteriology, 204 (1),1-18(2022)

9- Sheela C. , Kazim A., Madhumita K., " Optimization of indole acetic acid production by isolated bacteria from Stevia rebaudiana rhizosphere and its effects on plant growth" , Journal of Genetic Engineering and Biotechnology,16, 581-586(2018)

10- Ananthalakshmi S., Therese J.P. and M.Gowri M., " Complexation behaviour of 3- indole acetic acid with dipositive metal ions and the characterization of the complexes" , INTERNATIONAL JOURNAL OF PHARMACY & LIFE SCIENCES, 4(5), 2638-2643(2013)

11- Alexander A. K., Alexei G. S., Petros A. T.; Moschos G. P., and Yurii D. P.," Complexation of Indole-3-acetic Acid with Iron(III): In¯uence of Coordination on the p-Electronic System of the Ligand" , Monatshefte für Chemie , 132 , 675-681 (2001)

12- Ksenia S.- B. ,Anna S. ,Monika L. Daniel G., Oliver O. , Magdalena M.- G. , Danuta M. , Barbara M.-O.," New Zn(II) coordination polymer of indole-3-acetic acid, a plant-growth promoting hormone: Crystal structure, spectroscopic characterization, DFT calculations and microbiological activity" , Polyhedron, 185 (2020)

13- Moamen S. R., Ali S., Meshari M. A. ," Synthesis of Al(III), Bi(III), Sb(III), Sn(II) and Pb(II) Complexes Based on a Plant Auxin Hormone: Characterization; DFT, Pharmacokinetics and MOE-Docking with Plant-Cell Proteins", Chemistry Europe, 6(16), 3813-4033(2021)

14-Muhammad I., "Boron-centred soft ligands and their complexes with Na, K, Bi(III) and Pb(II) ions - An approach towards inexpensive luminescent materials", Ph.D.Thesis, Universität Bielefeld, Pakistan(2014)

15-Swiatoslaw T., "Scorpionates II: Chelating borate ligands", Imperial College Press, London WC2H 9HE (2008)

16- Ahlam J. A. and Asmaa M. N. K. "Preparation and Characterization of Di-, Tri-, and Tetranuclear Schiff Base Complexes Derived from Diamines and 3,4-dihydroxybenzaldehyde"**,** Bioinorganic Chemistry and Applications**,** vol.2013,1-14 (2013)

17- Silverstein R. M. and Webster F. X., "Spectrometric Identification of Organic Compounds", John Wiley and Sons, New York, NY, USA, 6th edition, 1997.

18- Dudley W. and Ian F., "Spectroscopic methods in organic chemistry", 6th edition, McGraw-Hill (2008)

19- Kamnev A.A, Shchelochkov A.G., Perfiliev Y.D., Tarantilis, P.A. Polissiou M.G., " Spectroscopic investigation of indole-3-acetic acid interaction with iron(III)", Journal of molecular structure, 563-564, 565-572 (2001)

20- Saja A.J.* and Asmaa M. N. K.," Characterization and synthesis of new Schiff base compound from levofloxacin and L-cysteine with its Cu(II) and Pt (IV) complexes and estimation antibacterial and antifungal activities ", Biochem. Cell. Arch. Vol. 21, Supplement 1, pp. 2187-2195 (2021)

21- Ganesh N. N., Aishakhanam H. P., Raghavendra P. B., Shashikala G. L. and Kalagouda B. G., " Rare Earth Complexes of Indole-3-Acetic Acid Derived Schiff Base: Synthesis, Characterization and Plant Growth Activity ", Chemistry Journal, Vol. 03, Issue 06, pp. 149-157 (2013)

22- Ahlam J. A.-G. and Asmaa M. N. K."Synthesis and Characterization of New Schiff Bases Derived fromN (1)-Substituted Isatin with Dithiooxamide and Their Co(II), Ni(II), Cu(II), Pd(II), and Pt(IV) Complexes", Bioinorganic Chemistry and Applications

Vol. 2009, 1-12 pages (2009)

23- Lever A. B. P., *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam,The Netherlands, 1968

24- Anacona J. R., Johan C., and Ovidio A. A. , " Synthesis, Spectroscopic, and Magnetic Studies of Mono- and Polynuclear Schiff Base Metal Complexes Containing Salicylidene-Cefotaxime Ligand", International Journal of Inorganic Chemistry , Volume 2013 , 7 pages (2013)